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Supreme Court of the United States

OCTOBER TERM, 1938

No. 441

THE ELECTRIC STORAGE BATTERY CO.,
PETITIONER,

vs.

GENZO SHIMADZU AND NORTHEASTERN ENGINEERING CORPORATION

ON WRIT OF CERTIORARI TO THE UNITED STATES CIRCUIT COURT OF APPEALS FOR THE THIRD CIRCUIT

PETITION FOR CERTIORARI FILED OCTOBER 27, 1938.

CERTIORARI GRANTED DECEMBER 5, 1938.

INDEX TO EXHIBITS.

Patented May 11, 1926. 1,584,149

UNITED STATES PATENT OFFICE.

GENZO SHIMADZU, OF KYOTO, JAPAN.

METHOD OF MANUFACTURING METAL POWDER.

No Drawing. Application filed January 30, 1922. Serial No. 532,220.

The present invention relates to a method of manufacturing fine powder of a plastic metal, by putting the plastic metal such as lead, in pieces in a rotatable vessel, and rotating the vessel so as to cause friction of the metal lumps with each other and with the inner surface of the vessel thereby effecting the abrasion of the metal pieces. The object of this invention is to manufacture spongy chemically re-active, fine lead powder by a simple and cheap process without crushing the same as has hitherto been the case.

Hitherto, the manufacture of metal powder has been done either by crushing or grinding the material or by a method, as in the case of manufacture of zinc dust, which consists in cooling a mixture of zinc vapour with air so that the metal coagulates into a fine powder.

The products of these old processes, however, are coarse-grained and liable to harden on the surface layer. Besides, while the particles of the powder obtained by crushing or grinding are generally pressed flat and are therefore with difficulty acted upon by chemicals, the powder obtained by atomizing and cooling process is only a relatively coarse product, which is not chemically reactive. Also the powder which is obtained by filing is not only coarse-grained, but is liable to be impaired in its purity by the mixture of the particles which wear off from the files themselves.

Thus the former products are not best adapted for use in special chemical purposes, which are aimed at in the present invention.

The present invention consists in rotating a rotatable vessel, containing lumps of metallic lead, in such a manner that the metal lumps rub against one another, and the inner surface of the vessel, causing abrasion and pulverization of the lumps. The degree of fineness of the powder can be regulated by regulating the quantity of the metal lumps put in the vessel.

To give a practical example of manufacturing lead powder according to the present invention;

A circular hollow cylinder made of iron, 60 inches in diameter and 60 inches in length, is horizontally and revolubly mounted. Within this cylinder is fitted an air-blower provided with small holes. Through one end of the cylinder is provided an orifice for feeding it with the material, and at the other end, an orifice to discharge the product.

The cylinder is, at the start, filled with 500 balls of steel, 1 inch in diameter, together with 1,000 kilograms of lead balls of 1.5 inches in diameter. As the abrasion is going on, the cylinder is replenished with lead ball continuously and at a definite speed at a rate of 100 kilograms an hour, while air blast having a pressure of 2.5 pounds per square inch, is sent out of the air-blower. The cylinder is caused to rotate at a rate of 15–25 times per minute. On account of this rotation of the cylinder, the lead balls contained therein get abraded and pulverized into very fine powder, which is blown out of the cylinder through the discharge orifice by means of the air blast from the said blower, and the lead powder thus blown out is led into a suitable chamber and collected there. By this operation, 100 kilograms per hour of fine powder with an apparent specific gravity of about 2.1 is obtained. The above described arrangement may be modified, and instead of providing a separate discharge passage, the cylinder body may be pierced through all over with small holes, whence the powdered product may be blown out to be collected in any suitable chamber.

The lead powder thus obtained is very fine and has an extensive surface so that its apparent specific gravity may be made, in some cases, even smaller than 1. It easily oxidizes and spontaneously ignites, so that it is necessary to provide with a cooling apparatus to radiate the heat generated by friction, when treating easily oxidizable metals, such as lead.

In short, the present invention does not crush, grind or file metals, but reduces them into powder by abrasion, pieces of the metal to be pulverized being put in a slowly rotating vessel, and caused to rub against one another and the wall of the vessel. The principal advantages of my invention over the hitherto known processes are as follows:—

1. A small amount of power is required; the process is simpler; and the fineness of the product can be regulated as desired.

2. A very high degree of fineness can be attained, without impairing the purity of the product.

3. The product being spongy and having

extensive surface, has a strong chemical reactivity. It often oxidizes in the air and spontaneously ignites. It is therefore most suitable for chemical purposes and is economical too.

4. The product oxidizes at a low temperature, but its catalytic action is very strong due to its extensive surface and consequently is very useful as a catalyzer, a depolarizer of electric battery, a reducing agent, or as an oxygen carrier.

Claims.

1. A method of forming a finely divided chemically reactive lead powder of such fineness and activity as to be readily changed chemically on contact with air, which comprises introducing relatively large masses of lead into a rotatable vessel, rotating said vessel at a relatively low speed and forming said lead powder by attrition of said lead masses resulting from the rubbing of said masses against each other.

2. A method of forming a finely divided chemically reactive lead powder of such fineness and activity as to be readily changed chemically on exposure to air, which comprises introducing relatively large masses of lead into a rotatable vessel, rotating said vessel at a relatively low speed, introducing a current of air into said vessel, forming said lead powder by attrition of said lead masses resulting from the rubbing of said lead masses against each other, and removing the said powder from said vessel by means of said current of air.

In testimony whereof I have affixed my signature.

GENZO SHIMADZU.

Patented May 11, 1926. 1,584,150

UNITED STATES PATENT OFFICE.

GENZO SHIMADZU, OF KYOTO, JAPAN

PROCESS OF MANUFACTURING POWDER OF LEAD SUBOXIDE INTERMINGLED WITH POWDER OF METALLIC LEAD.

No Drawing. Application filed July 14, 1923. Serial No. 651,821.

This application is a continuation in part of application Number 431,473, filed Dec. 17, 1920.

This invention relates to a process of manufacturing a very fine powder of lead suboxide intermingled with powder of metallic lead, consisting in putting pieces of metallic lead in a rotatable vessel, keeping the same at a temperature not less than 60° C., introducing into the vessel, while slowly rotating, air or any gas containing oxygen, or any other oxidizing agent, causing thus the surface of the pieces of metallic lead to oxidize lead-suboxide, and reducing the suboxide thus formed into a very fine powder by abrasion. The object of this invention is to obtain a large quantity of a very fine chemically reactive powder the principal part of which is lead suboxide, by promoting reduction of the metallic lead pieces into powder by abrasion by converting the surface of the pieces to suboxide.

This invention consists in putting in a rotatable vessel pieces of metallic lead, keeping these pieces at a temperature not less than 60° C., and while rotating the vessel sending air, or other gas containing oxygen thereinto, or sending any other oxidizing agent thereinto, thus oxidizing the surface of the pieces of lead and reducing them by abrasion into a very fine powder which is chemically very reactive.

In this invention the surface of the material, that is, metallic lead, is caused to be acted upon by the air or other oxidizing agent, and to be covered with a coating of lead-suboxide, which being brittle and lacking tenacity compared with metallic lead, can be easily and quickly reduced into powder by abrasion. And as soon as a new metallic surface of the pieces appears, it will be instantly oxidized and abraded, thus continuously producing the desired powder. Thus, the efficiency of manufacture is very great, and the product is a very fine oxidized powder of lead, which is chemically very reactive, intermingled only with a little coarse-grained powder.

The product of this invention is so fine that the apparent specific gravity is 1–3. The composition of powder is approximately from 93 to 97% lead suboxide and about 3 to 7% metallic lead. It is a porous mass of amorphous particles and although not very much different in its property from metallic lead, it is so chemically reactive that it is spontaneously converted into litharge by merely exposing it to air. If a drop of water is dropped on a pile of the same, or a lighted match is applied thereto, oxidation is started instantly, and by the reaction heat the oxidation continues until the whole is converted into litharge.

I am aware that there is known a process of manufacturing lead oxide by putting pieces of lead converted into monoxide or litharge in a rotatable drum, and excoriating the same. Another method known is to heat lead in a closed vessel to a point nearly approaching the melting point in presence of oxidizing agent and thus making lead oxide by heating. But these have nothing to do with the manufacture of lead suboxide, and it is evident that the object of these processes is quite different from that of the present invention, as lead suboxide resembles in its chemical and physical properties rather to metallic lead than to lead oxides; and I need not say that lead suboxide is quite different from other oxides of lead in brittleness, ductility &c., which are principal factors in reducing a substance into powder.

I will now give an example of putting my invention into practice.

Mount rotatably in a horizontal position an iron cylinder about 60 inches long with a diameter of about 60 inches pierced all over with holes 1/8 of an inch in diameter at a rate of four holes in one inch square, and put therein balls of metallic lead about one inch in diameter and also balls of steel or any other hard substance of about the same size. Provide the cylinder, or drum, with pipes to blow air thereinto. Now turn the cylinder at a rate of 25 times in one minute, blowing air thereinto all the while, and keeping the temperature within the cylinder at 60 to 200° C. Then the surface of lead balls will gradually be oxidized by the air, and they will be covered with a layer of lead suboxide, which is comparatively brittle and will be abraded into a fine powder. The metallic surface of the lead balls exposed by the rubbing off of the layer of lead suboxide formed thereon, will be acted upon by air and being oxidized a layer of lead suboxide will be again formed which will be abraded off again as before. Thus, by oxi-

dizing lead balls and abrading off the layer of lead suboxide thus formed, a fine powder can be very easily manufactured. The powder thus formed may be discharged from the holes on the wall of the cylinder.

In this invention, as an oxidizing agent, oxygen, hydrogen peroxide, ozone or a gas containing any of them, or anything that oxidizes the surface of metallic lead, may be utilized besides air. Any such oxidizing agent may be blown into the cylinder in a gust, or may cause the cylinder to suck it. If it is blown into, it is convenient to utilize the force of the current thus caused to blow the powder formed out of the cylinder, and then collect it.

Again, in this invention, in heating lead balls, friction heat or reaction heat caused by oxidation of lead, or both may be utilized; or heat may be introduced from an electric heater, gas heater, or any other source. The main point is to maintain the material lead in the atmosphere of air or any other oxidizing gas at a temperature of not less than 60° C. And in the case of utilizing friction or reaction heat that arises while working this invention, it is preferable to provide around the rotating cylinder heat insulating appliance to prevent the radiation thereof. Also it goes without saying that the production of heat in this case may be regulated by adjusting the weight of metallic balls, thus reducing or increasing friction surface and pressure, or by increasing or reducing the number of rotations of the cylinder.

The advantages of this invention may be enumerated as follows:—

(1) It is easy to maintain the harmony of oxidation of the surface of the material lead, and abrasion of oxidized lead; and a large amount of a fine powder of lead suboxide intermingled with powder of metallic lead, which does not practically differ in its properties from a fine powder of metallic lead, is obtained without using much powder.

(2) The rate of mixture of powder of metallic lead and that of lead suboxide, the apparent specific gravity, and condition of particles, of the product may be altered by adjusting temperature, gust of oxidizing agent, &c.

Claims:

1. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in putting pieces of metallic lead in a rotatable vessel in a dry state, introducing into the said vessel currents of an oxidizing gas to oxidize the surface of the lead while rotating the said vessel, and abrading off the oxide formed on the surface.

2. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in putting in a rotatable vessel pieces of metallic lead in a dry state, introducing into the said vessel while rotating blasts of a gas containing oxygen, such as air, causing such blast to blow the powder produced out of the vessel.

3. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead comprising in putting pieces of metallic lead in a dry state into a rotatable vessel, and delivering an oxidizing gas into the vessel while revolving the same.

4. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in putting in a rotatable vessel pieces of metallic lead in a dry state, and rotating the vessel maintaining the temperature within the vessel at not less than 60° C., at the same time introducing into the vessel an oxidizing gas.

5. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in providing a rotatable vessel with a heat insulating means, putting in the vessel pieces of metallic lead in a dry state, and rotating the vessel maintaining the temperature of the lead at 60–200° C. and introducing into the vessel an oxidizing gas.

6. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in putting in a rotatable vessel pieces of metallic lead, introducing air thereinto and rotating the vessel maintaining the temperature of the material at not less than 60° C. by the heat generated by friction and chemical reaction.

7. A process of manufacturing a fine powder of lead suboxide intermingled with powder of metallic lead, comprising in putting in a rotatable vessel pieces of metallic lead and balls of steel, and rotating the vessel maintaining the temperature of the contents of the vessel at not less than 60° C., at the same time introducing air into the vessel, thus causing oxidation and abrasion to take place.

8. In the production of a finely divided mixture of lead suboxide and metallic lead, the step of tumbling together and agitating, a mass of hard heavy material containing metallic lead, while maintained at a temperature betweer about 60° C. and about 200° C.

9. A method of forming a finely divided powder containing a large proportion of oxidized lead which comprises impinging a current of air on lead masses in a dry state, abrading the lead masses, and controlling the temperature to obtain a finely divided powder containing a large proportion of oxidized lead.

10. A method of forming a finely divided

powder containing a large proportion of oxidized lead which comprises impinging a current of air on lead masses in a dry state, and controlling the temperature to maintain the temperature above 60 degrees C. to obtain a finely divided powder, containing a large proportion of oxidized lead.

11. A method of forming a finely divided powder containing a large proportion of oxidized lead which comprises impinging a current of air on lead masses in a dry state, abrading the lead masses, and controlling the current of air to obtain a finely divided powder, containing a large proportion of oxidized lead.

12. A method of forming a finely divided powder containing a large proportion of oxidized lead comprising impinging a current of air on lead masses in a dry state, abrading the lead masses, and controlling the temperature and current of air to obtain a finely divided powder containing a large proportion of oxidized lead.

13. A method of forming a finely divided powder containing a large proportion of oxidized lead which comprises impinging a current of air on lead masses in a dry state, and controlling the current of air and the temperature to maintain the temperature above 60 degrees C. to obtain a finely divided powder containing a large proportion of oxidized lead.

14. Comminuted lead-lead suboxide mixture with apparent specific gravity 1 to 3.

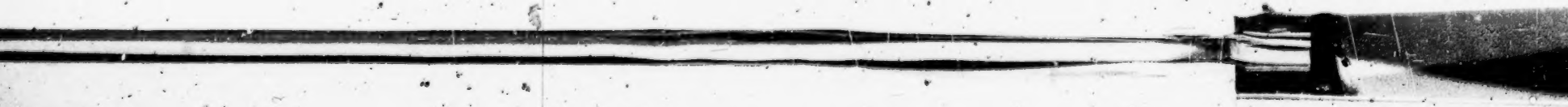
15. As a new composition of matter, a highly chemically reactive finely divided powder comprising a major portion of lead suboxide, said powder being capable of spontaneous oxidation.

16. As a new composition of matter, a highly chemically reactive powder, comprising a large portion of lead suboxide, said powder being capable of spontaneous reaction on contact with moisture.

17. As a new composition of matter, a highly chemically reactive powder, comprising a large portion of lead suboxide, said powder being capable of spontaneous reaction on contact with air.

In testimony whereof I have affixed my signature.

GENZO SHIMADZU.



Patented May 11, 1926. 1,584,151

UNITED STATES PATENT OFFICE.

GENZO SHIMADZU, OF KAMIKYO KU, KYOTO, JAPAN.

PROCESS OF MANUFACTURING LEAD OXIDE.

No Drawing. Application filed April 18, 1924. Serial No. 707,509.

This application is a continuation in part of application Number 431,473, filed December 17, 1920.

This invention relates to improvements in the process of manufacturing lead oxides and consists in oxidizing fine lead suboxide powder intermingled with metallic lead powder by the initial application of heat and without fusing the lead suboxide. The object of this invention is to simplify the process thereby economizing the labour and expenses of manufacture, and at the same time to obtain lead oxides, such as litharge, red lead or the like, in a pure state and in a special form, best adapted for the purposes for which they are generally used.

There are known various processes of manufacturing lead oxides by oxidizing fine powder of lead, but in all these known processes, lead powder must either be continuously heated or treated with steam, or an oxidizing a[illegible]t is used to accelerate the oxidation. Thus the work is troublesome, and the product is not pure.

Now, this invention removes all these drawbacks, and consists in taking pieces of metallic lead into a revolvable drum, and revolving the drum slowly at a rate of about twenty-five revolutions per minute, blowing the air into the drum all the while. Then the heat generated by friction and oxidation (within the drum) of the lead pieces will raise the temperature within the drum and maintain it at not less than 60° C. The friction too will form new metallic surface on the lead pieces, which as soon as formed will be converted into lead suboxide by the heat and the oxygen in the air. The film of lead suboxide thus formed will be reduced to powder by abrasion, but not by lead pieces striking against one another, like in the case of a common tube mill or ball mill. When the lead suboxide film is abraded off, a new metallic surface will be formed, which as soon as formed will be abraded off as before, thus continually producing fine powder of lead suboxide intermingled with metallic lead powder directly and in dry condition. The lead suboxide powder intermingled with metallic lead powder thus obtained is so fine and chemically active that if a lighted match be applied to part of its pile or a few drops of water be dropped on it, oxidation will instantly commence, igniting it briskly as if it were burning sulphur or such easily inflammable substance. Thus, if care be taken that the material does not fuse, the whole of it shall be instantly converted into powder of lead monoxide without supplying any more external heating or using any oxidizing agent other than air. And if fresh supply of lead suboxide powder be piled upon small remainder of the actually oxidizing lead suboxide powder, the ignition may be perpetually maintained.

The lead suboxide powder intermingled with metallic lead powder produced according to this invention is extremely fine, porous and spongy, its apparent specific gravity being not more than 1–3. It is chemically very active, sometimes starting spontaneous ignition in the air. If it comes into contact with water or moisture, it generates a great heat, and instantly turns into lead monoxide, lead hyroxide, basic lead hydroxide, or the like; and as it becomes red-hot by the reaction heat rising, it becomes chemically very reactive. It is very reactive, but is not unstable like lead suboxide powder manufactured chemically by reducing lead oxalate, and is therefore very convenient to handle industrially as a material.

Sometimes lead suboxide intermingled with a small proportion of metallic lead powder, may be left exposed to the atmosphere from two to four weeks, and the powder will be converted into litharge, being oxidized directly by the oxygen in the air.

The litharge thus obtained can be turned into red lead, as is commonly practiced, by heating the same in a furnace, or a pan at a temperature not more than 500° C.

Thus this process is economical, because heat is necessary only to start oxidation at a part of the material, and the reaction heat does the work of oxidizing the rest. It is very simple and saves much labour. Also, as it is simple there is little chance of impurities getting into the product. If we select pure lead pieces for material, we shall be able to obtain pure powder not containing any other metal, from which we can manufacture litharge and red lead purer than those now on the market. Moreover, the product obtained by my process has different properties from lead oxides obtained by known processes, that is, by continuous heating or the use of a chemical agent to accelerate oxidation. It is more porous and lighter in the apparent specific gravity, such properties depending upon fineness of the lead suboxide powder which can be regu-

lated at will. Thus, the litharge or red lead manufactured according to my process is an ideal material as the paste for lead accumulators on account of its purity and the properties mentioned above. Used as paint, it has a higher consistency and extensibility and is rich in covering power.

I claim:

1. The process of forming finely divided oxygenated lead compounds which comprises treating a finely divided chemically reactive powder comprising a major portion of lead suboxide with an oxidizing substance.

2. The process of forming a finely divided oxygenated lead compound which comprises treating a finely divided chemically reactive powder comprising a major portion of lead suboxide with an oxidizing substance, and maintaining the reaction by the evolved heat of reaction.

3. The process of forming a finely divided oxygenated lead compound which comprises treating a finely divided chemically reactive powder comprising a major portion of lead suboxide with an oxygen containing substance and continuing the reaction by the evolved heat of reaction.

4. The method of forming finely divided lead oxide which comprises treating a finely divided chemically reactive powder comprising a large proportion of lead suboxide and a minor proportion of metallic lead with air, and continuing the reaction by the evolved heat of oxidation.

5. The method of forming a finely divided oxygenated lead compound which comprises contacting finely divided chemically reactive powder comprising a large proportion of lead suboxide with moisture and continuing the reaction by the evolved heat of reaction.

6. The process of forming higher oxides of lead which comprises treating a finely divided chemically reactive powder comprising a major portion of lead suboxide with an oxidizing substance to form lead monoxide, and oxidizing said lead monoxide to such higher oxides of lead.

7. The process of forming higher oxides of lead which comprises treating a finely divided chemically reactive powder comprising a major portion of lead suboxide with an oxidizing substance, maintaining the reaction by the evolved heat of reaction to form lead monoxide and oxidizing said monoxide to said higher oxides of lead.

In testimony whereof I have affixed my signature.

GENZO SHIMADZU.

Patented May 11, 1926. 1,584,152

UNITED STATES PATENT OFFICE.

GENZO SHIMADZU, OF KAMIKYO KU, K.OTO, JAPAN.

PAINT.

No Drawing. Application filed April 18, 1924. Serial No. 707,510.

This case is a continuation in part of application Number 532,725, filed January 30, 1922, and a continuation in part of application Number 431,473, filed December 17, 1920.

This invention relates to a paint, consisting of lead suboxide powder intermingled with powder of metallic lead of a very small apparent specific gravity combined with boiled oil, or a mixture of boiled oil and resin, or any other vehicle generally used in paints, and the object thereof is to obtain a paint having a great covering capacity and extensibility, at the same time acting as an anti-corrosive as well as anti-fouling paint, the chemically reactive force of lead suboxide powder being utilized for the latter purposes.

The lead suboxide powder used in this invention is obtained in dried condition by abrading mechanically successive films formed on lead pieces exposed to the air and kept at a temperature not less than 60° C. The lead suboxide powder intermingled with metallic lead powder thus obtained has special properties different from those of lead suboxide hitherto known, and is spongy and porous, having an apparent specific gravity of 1–3. Exposed to water or moisture, it is instantly converted into lead monoxide, lead hydroxide or basic lead hydroxide. It is so chemically reactive that if a few drops of water be dropped on a pile of it, or a lighted match be applied thereto, it ignites as if it were sulphur or such easily inflammable substance, until the whole of the pile is converted into litharge. The lead suboxide powder intermingled with metallic powder used in this invention is thus chemically very active but is not unstable as such powder manufactured chemically by reducing lead oxalate, and is very convenient to handle and preserve for industrial purposes. It is of such special qualities, and used in the place of red lead, it proves not only to be a very efficient pigment, but is also anti-corrosive and anti-fouling on account of its reducible and poisoning properties.

To show an example of carrying my invention into practice, round pieces of lead are put in a revolvable drum together with steel balls, and the drum is slowly revolved, introducing thereinto air or any other oxidizing gas. Then the heat generated by friction and oxidation of the lead pieces will keep the interior of the drum at a temperature not less than 60° C., and films of lead suboxide will be formed on the face of the lead pieces. The films of lead suboxide successively formed on the lead pieces are successively abraded off, and a very fine and chemically reactive lead suboxide powder intermingled with a small proportion of powder of metallic lead is produced. Such powder is then mixed with boiled oil, varnish vehicle, solution of casein, cellulose esters, lacquers, or any other vehicle of paints, and is kneaded; and a paint of a suitable consistency will be obtained. When the paint of my invention is spread over the surface of iron or any other metal, or wood, and exposed to the air, it gets gradually oxidized in a natural way as the vehicles dries, forming finally a compact layer of oxide just like one formed spontaneously on the polished surface of a metal, and serves as a very efficient protective film. The surplus lead suboxide and metallic lead act as a strong poison against living organisms, such as shell fish, worms, insects, sea-weeds, and bacteria, and serves to prevent their attachment.

The paint of my invention possesses, moreover, a covering capacity and an extensibility several times greater than ordinary red lead paint. It makes, therefore, a very efficient and convenient anti-corrosive and anti-septic paint, it being especially efficient and economical for painting the ship's bottom, because with my paint one need not go through the trouble of giving to the ship first an anti-corrosive coating, and then when it has dried, a second coating of anti-fouling paint, but only one coating efficiently attains the two objects.

The inventor is aware that powder of lead suboxide, or metallic lead, is used as a material of paints, but the lead suboxide powder intermingled with metallic lead, used in this invention has characteristics quite different from those of hitherto known lead suboxide, or metallic lead, powder, and by using the powder having such special characteristics, the inventor has been enabled to secure special efficiency. It is firmly believed that this application therefore constitutes a new invention.

Claims.

1. A paint comprising a vehicle and a finely divided chemically reactive powder containing a major proportion of lead sub-

oxide and a minor proportion of metallic lead, said powder resulting from the impingement of a current of air on relatively large masses of lead in a dry state, subjecting the lead to surface attrition, controlling the temperature to cause the formation of lead suboxide in the said proportions, and carrying of the powder resulting from the above by the said current of air.

2. A paint comprising a vehicle and a finely divided chemically reactive powder containing a major proportion of lead suboxide and a minor proportion of metallic lead, said powder resulting from the impingement of a current of air on relatively large masses of lead in a dry state, subjecting the lead to surface attrition, controlling the temperature to be not less than sixty degrees centigrade, so as to form powder containing lead suboxide in the above proportions and carrying of the powder so formed by the above mentioned current of air.

In testimony whereof I have affixed my signature.

GENZO SHIMADZU.

Patented May 11, 1926. 1,584,479

UNITED STATES PATENT OFFICE.

GENZO SHIMADZU, OF KYOTO, JAPAN.

PROCESS OF MAKING PLATES FOR STORAGE BATTERIES USING LEAD SUBOXIDE.

No Drawing. Application filed February 20, 1923. Serial No. 620,267.

This invention relates to a process of manufacturing plates for storage batteries characterized by using as the principal active material lead suboxide (Pb_2O), mixing the same with water or dilute sulphuric acid, kneading the mixture and coating or filling in the plates or grids with the paste thus formed. The object of this invention is to obtain durable plates for storage batteries by causing the lead suboxide to convert easily to hydroxide while drying.

Plates for storage batteries, according to methods hitherto known, are generally manufactured by coating or filling in the plates or grids with a paste formed by kneading a lead oxide, such as litharge minium, together with dilute sulphuric acid, but in such method, the chemical change that occurs in the lead oxide, and the drying of the paste must be so regulated that they progress parallel. Otherwise, the paste, losing its volume by drying, will crack, and interspaces will be formed between the coating and the plate or grid, thus shortening the life of the battery. Moreover, when drying the paste, as it does not undergo any structural change, as hardening of cement by hydration, it is very difficult to make batteries that last long.

According to this invention, a very fine and spongy lead suboxide of an apparent specific gravity of not more than 3 is utilized as active material, and is applied to the plate, or grid, after kneading the same in water or dilute sulphuric acid, into a paste. After application to the plate or grid and when drying, such paste will be acted upon by water and oxygen in the air, and will be converted into lead hydroxide and will increase its volume which, counteracting the shrinkage due to drying, removes the drawback of cracking. Moreover, when the suboxide is converted into hydroxide, a marked change in the construction of the paste takes place and the paste hardens in the same condition as cement hardens by hydration, and thus very durable batteries can be manufactured.

The lead suboxide used in this invention, is formed by reducing metallic lead into fine, spongy powder by mechanical abrasion. It is chiefly composed of lead suboxide, but is sometimes intermingled, from the nature of the process to manufacture it with 1 to 40% metallic lead powder. Also, from the nature of lead suboxide, it is slowly converted, while being manufactured or when it is left exposed to the air, into monoxide, and consequently it is sometimes intermingled with lead monoxide. But such lead monoxide formed by oxidation in a warm room in the atmosphere retains, different from monoxide formed by igniting lead powder, an apparent specific gravity of the suboxide used as the material, easily hardens, is rich in activity and forms a durable plate. Consequently, even when lead suboxide is slowly oxidized while it is stored, such oxide in no way obstructs the carrying of this invention into effect.

Thus, in my invention, the lead suboxide used as material, is manufactured without using any water; there is little chance for any impurities to intermingle therewith during the process of manufacture; and there is no necessity of adding to the lead suboxide when kneading the same into paste in order to lengthen the life thereof any drug prejudicial to batteries. Moreover, the process of "forming" may be entirely dispensed with, plates being "formed" when the battery is charged with electricity for the first time. Of course, the process of "forming" may be carried out according to the ordinary method.

To explain my invention more in detail, the following is an example of carrying it into practice:—

Pieces of metallic lead are reduced to fine powder by causing the pieces to rub against one another in a slowly revolved drum, and the powder is then exposed to the air. Then take 300 grammes of such powder, which is very fine and light, having an apparent specific gravity of not more than 3, mix it with 45 cubic centimeters of water, knead the mixture and with the paste thus formed coat or fill the ordinary plates or grids. When the plates are dry, they are ready to be used for storage batteries. Apparent specific gravity is measured by filling a vessel of known capacity with lead suboxide powder by causing the powder to fall from a sieve, smooth the surface softly without pressing, and weigh it. Then, take weight of water of 4° C. of the same volume,

and divide the weight of the former by that of the latter, and the quotient is the apparent specific gravity sought.

Claims:

1. The process of preparing plates for storage batteries, which consists in reducing metallic lead to a fine powder, exposing said powder to the air, mixing the same with liquid, kneading the mixture into the form of a paste, coating the plates with said paste, and drying the same thereby to convert the lead suboxide into lead monoxide and lead hydroxide.

2. The proces of preparing plates for storage batteries, which consists in reducing metallic lead to a fine powder, exposing the same to the air, mixing 300 grammes of said powder with 45 cubic centimeters of water, kneading the mixture to form a paste, coating the plates with said paste, and drying the same thereby to convert the lead suboxide into lead monoxide and lead hydroxide.

3. A process of manufacturing plates for storage batteries, consisting in kneading lead suboxide intermingled with lead monoxide and sufficient liquid to form a paste and applying the same to or filling therewith the plates or grids.

4. A process of manufacturing plates for storage batteries, consisting in kneading lead suboxide intermingled with lead monoxide, metallic lead, and sufficient liquid to form a paste, and applying the same to or filling therewith the plates or grids.

In testimony whereof I have signed my name to this specification.

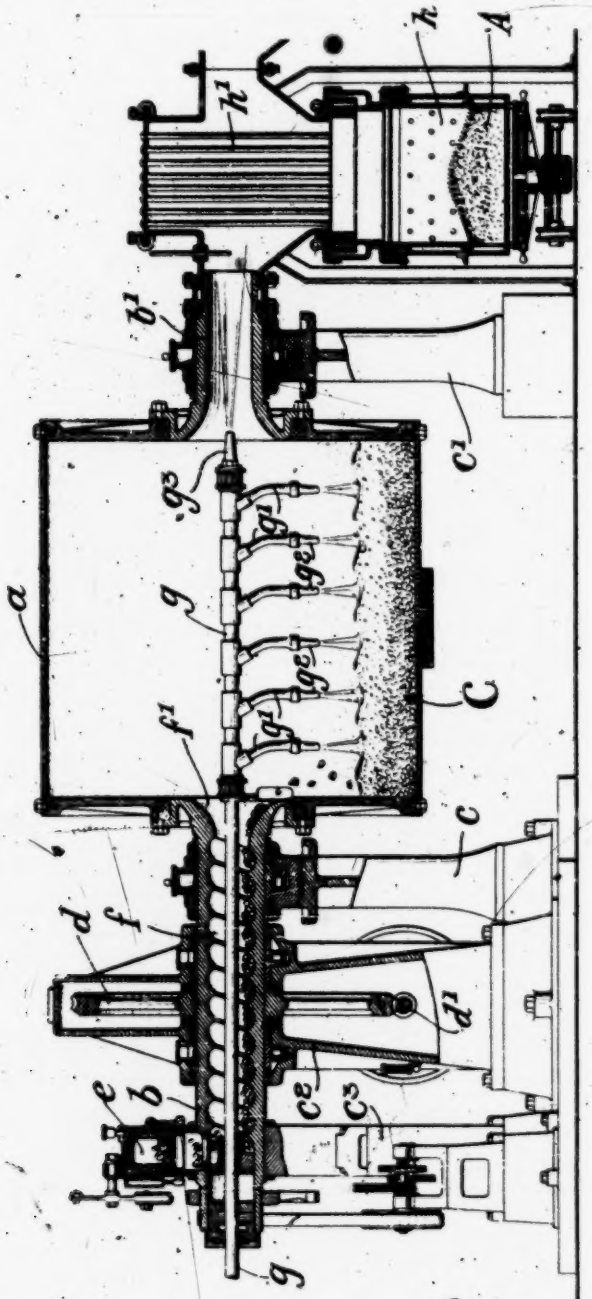
GENZO SHIMADZU.

Jan. 31, 1933. G. SHIMADZU 1,896,020

APPARATUS FOR THE CONTINUOUS PRODUCTION OF LEAD OXIDES IN THE DRY STATE

Original Filed April 27, 1926 2 Sheets-Sheet 1

Fig. 1.



G. Shimadzu
Inventor

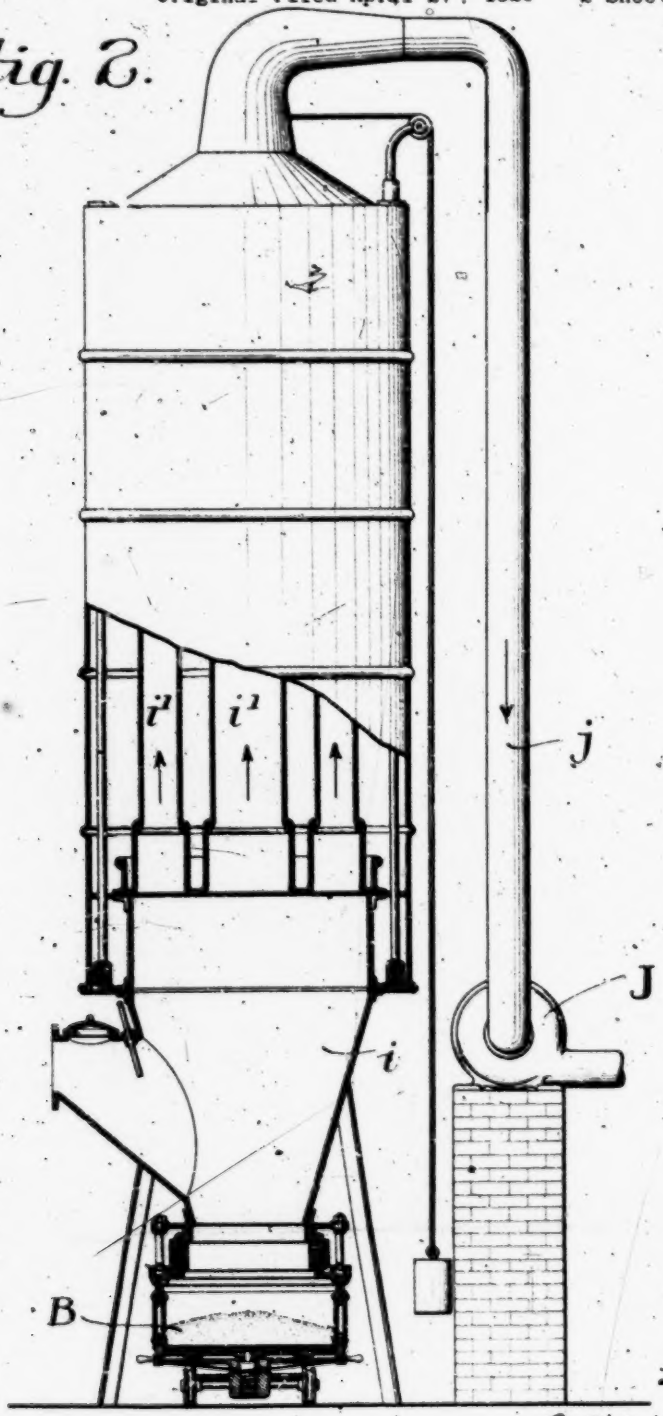
By Marks & Clerk
Attys

Jan. 31, 1933. G. SHIMADZU 1,896,020

APPARATUS FOR THE CONTINUOUS PRODUCTION OF LEAD OXIDES IN THE DRY STATE

Original Filed April 27, 1926 2 Sheets-Sheet 2

Fig. 2.



G. Shimadzu inventor

By: Marks & Clark Attys

Patented Jan. 31, 1933 1,896,020

UNITED STATES PATENT OFFICE

GENZO SHIMADZU, OF KIOTO, JAPAN

APPARATUS FOR THE CONTINUOUS PRODUCTION OF LEAD OXIDES IN THE DRY STATE

Application filed April 27, 1926, Serial No. 104,998. Renewed June 21, 1929.

This invention relates to an apparatus for the continuous production of lead oxides, the object of the invention being to obtain such oxides in the form of extremely fine powders and in a dry state.

The invention involves the subjection of pieces of metallic lead maintained in a state of agitation to artificially supplied atmospheric air or other oxidizing gas whereby a film or coating of oxide will be formed on the pieces, the formation of the film or coating being augmented without fusion of the metal by the heat generated in the principal reaction between metallic lead and the oxidizing gas and by the frictional heat created through rubbing of the pieces one against the other, this rubbing action causing also a brading off as a fine powder of the oxide thus produced and the oxidizing gas or a part thereof being also utilized to carry off the powder for collection and further treatment if needs be.

Broadly the apparatus of the invention comprises a vessel adapted to be rotated, means for feeding pieces of metallic lead thereto while the vessel is rotating, and means for artificially supplying atmospheric air or other oxidizing gas to the interior of the vessel in such a manner as to contact with the surfaces of the pieces of lead to oxidize the same and to take up and convey the formed oxide powder as it is abraded by the rubbing action of the pieces against each other to a collector and/or filter device.

In the appended drawings, I have shown an advantageous form of apparatus in which Figure 1 (horizontal section) represents an oxidizing chamber and Figure 2 (elevation with parts broken away), a dust catching tower.

Referring more particularly to Figure 1 of the drawings, *a* denotes a drum which for the purpose of permitting rotation is provided with trunnions *b*, *b'* supported by bearings *c*, *c'*. The trunnion *b* is also journalled in a bearing c^2 which is so designed as to form a casing for a worm-wheel *d* fast on the trunnion *b*, said worm-wheel being in mesh with a worm *d'* coupled to a suitable source of power.

The trunnion *b* is hollow and its interior is provided with helical grooves *f* which as the trunnion rotates function as a screw conveyor *f* which is supplied with pieces of lead by an automatic feeder *e*. Trunnion *f* conveys the pieces C' to the drum *a* into which they fall at *f'*.

Arranged axially in the hollow trunnion *b* is a stationary pipe *g* which extends into the drum *a* and is provided with downwardly directed branch pipes *g'* which may be provided at their ends, with nozzles g^2. The pipe *g* serves to supply atmospheric air or other oxidizing gas under relatively high pressure from a suitable source to the interior of the drum whilst the latter is rotating. The air or gas issuing from the nozzles g^2 impinges upon the lead pieces in the drum and acts primarily to cause a coating or film of oxide to be formed thereon. The trunnion *b'* is also hollow and the inner end of the supply pipe *g* is provided with a nozzle g^3 so arranged with respect to the interior of the trunnion *b'* as to form an ejector or exhauster for the drum *a*.

The oxide which in fact is a sub-oxide is formed on the pieces principally by the action of the oxidizing gas thereon as has been explained, the gas acting continuously on the surface of the pieces which are maintained in a state of agitation owing to the rotation of the drum so that all the pieces are properly subjected to the oxidizing action. This oxidation is aided by the heat generated by the reaction itself and also by the friction set up owing to the rubbing of the pieces one against the other. The oxide film or coating is of a comparatively brittle nature and the continual rubbing of the pieces together due to the rotational motion of the drum *a* causes this film or coating to be abraded off as a suboxide powder, thus exposing fresh surfaces of metallic lead to the action of the oxidizing gas and the other conditions which augment the formation of the oxide film. This abrading off or removal of the suboxide coating from the pieces of metallic lead is also caused in part by the impinging of the air from jets g^2 on the surfaces of the pieces of metallic lead. The air which is fed through pipe

g to the nozzles g^2 at relatively high pressure leaves the nozzles at a velocity sufficiently high to blow any oxide from those pieces of lead on which the air impinges. The combined rubbing action of the pieces and action of the jets of air upon the pieces of metallic lead provides a very efficacious means of reducing the oxide to a remarkably fine powder, so fine in fact that from tests made it has been proved that the weight of a given volume of the powder is only from one third to one tenth of the weight of the same volume of metallic lead, or less of the weight of the same volume of water. As a further proof of its fineness it is found that the sub-oxide powder will readily convert to litharge in the presence of an oxidizing agent by spontaneous oxidation after the application of initial heat. That is to say, if the heat of a match for example be applied momentarily to a quantity of the powder, the combustion will proceed of its own accord until all the powder has been converted to litharge.

The suboxide which is formed in my machine in the above described manner is a very unstable fine powder. It is essential that it be removed from the mill in which it is formed immediately after it has been ground or blown from the lumps of lead. Otherwise if it is permitted to remain within the mill for any appreciable length of time it will go over to litharge inasmuch as the temperature within the mill is sufficiently high and there is a plentiful supply of air present. In the arrangement shown the powder is removed substantially instantaneously after formation by the currents of air issuing from jets g^2 which penetrate the entire mass of lead and which leave the mill through trunnion b' carrying with it the formed powder. As will be noted the interior of trunnion b is flared from the drum to form a nozzle which, combined with the action of the air issuing from jet g^2, functions as an ejector to aid in the rapid removal of said powder. A chamber h is connected near its upper end to the hollow trunnion b' and acts to collect the powdered oxide or a portion of it issuing from the trunnion. This chamber h is provided with a plurality of vertical bars h' which act as a screen or sieve to break down the conveying action of the ejector by impingement of the particles thereagainst so that the particles will fall into the bottom of the chamber and accumulate therein as indicated at A. The sub-oxide powder may be removed as such from the chamber h at convenient intervals.

Frequently it is desirable that the product be in the form of litharge rather than suboxide. With the construction shown, the suboxide powder may be readily converted to litharge before removal from the container h. The advantage of converting the powder to litharge in this manner is that the conversion will be complete and the product will be uniform throughout due to the fact that the air within the chamber h is in heated condition and while so heated it has ready access to the powder as it falls on the pile a. Were the suboxide powder first permitted to accumulate in a pile and then oxidized it would be found that the product would not be uniform but that a large portion on the inside of the pile to which the air does not have ready access would remain in the suboxide state. To start the oxidation it is necessary to apply external heat to the product but once started the heat generated by the reaction will be sufficient to oxidize all of the powder which is thereafter formed in the mill and delivered to the chamber h. Any powder intermingled with gas that passes through the screen h' is transferred to a bag room or filter tower i where it is finally separated from the gas. This tower is provided with filter bags of suitable material such as silk which are subjected externally to a rarefied atmosphere or vacuum created in the upper part of the tower by means of the exhauster J. By this means the gas is drawn through the bags leaving the powder on the interior surface thereof from whence it falls and is collected at the bottom of the tower as indicated at B. Here again the sub-oxide powder may be removed as such at convenient intervals or first converted into litharge.

It will be appreciated that if found desirable a plurality of filter towers may be provided in series whereby the extracted gas may be subjected to further filtration to ensure complete separation of powder. It will also be appreciated that the provision of an initial separator h followed by a filter or filters is not essential to the carrying out of the invention. In some cases it might be found that the separator h could be dispensed with in which case the filter stage could be coupled direct to the drum. Again, the separator might in some instances be used without a filtration stage. I reserve to myself the right to such modification and others that are obvious in the construction and assembly of the apparatus.

I claim:

1. Apparatus for the production of lead oxides in the dry state, comprising a vessel adapted to be rotated, hollow trunnions supporting said vessel, a screw conveyer disposed in one of said hollow trunnions to introduce material into said vessel, an air pipe passing through said hollow trunnions and terminating in the other of said hollow trunnions whereby air passing through said pipe acts to expel dry material from said vessel through said other hollow trunnion.

2. Apparatus for the production of lead oxides in the dry state, comprising a vessel adapted to be rotated, hollow trunnions supporting said vessel, a screw conveyer dis-

posed in one of said hollow trunnions to introduce material into said vessel, an air pipe passing through said hollow trunnions and terminating in the other of said hollow trunnions whereby air passing through said pipe acts to expel dry material from said vessel through said other hollow trunnion; said air pipe having branches thereon provided with nozzles whereby air is also introduced into the interior of the drum.

3. Apparatus for the continuous production of lead oxides in the dry state, comprising a vessel adapted to be rotated, means for supplying oxidizing gas to the interior of the vessel, an outlet for said gas, and means comprising an injector for increasing the velocity of said gas as it passes through said outlet.

4. Apparatus for the continuous production of lead oxides in the dry state, comprising a vessel adapted to be rotated, means for feeding lumps of metallic lead to said vessel, a pipe for feeding air under pressure to said vessel a plurality of jets extending from said pipe to impinge upon said metallic lead pieces within said vessel whereby the surfaces thereof are oxidized, means for rotating said vessel to abrade said oxide from said surfaces by mutual attrition, and means for removing said oxide from said vessel substantially instantaneously upon formation.

5. Apparatus for the continuous production of lead oxides in the dry state, comprising a vessel adapted to contain pieces of metallic lead, means for feeding lead to said vessel, a pipe for feeding air under pressure to said vessel, a plurality of jets extending from said pipe to impinge upon the surfaces of said metallic lead pieces within said vessel, whereby the surfaces of said lead pieces are oxidized, means for rotating said vessel to cause said oxide to be abraded from said pieces by mutual attrition, said vessel having an outlet and means at the end of said pipe extending into said outlet for causing said air to pass through said outlet at a sufficiently high velocity to carry said abraded oxide from said vessel.

6. Apparatus for the continuous production of lead oxides in the dry state, comprising a vessel adapted to be rotated, means for feeding pieces of metallic lead to said vessel, a pipe for feeding air under pressure to said vessel a plurality of jets extending from said pipe to impinge against the surfaces of said lead pieces whereby said surfaces are oxidized and said oxide is blown from said pieces, and an ejector for removing said gas and said oxide from said vessel.

7. Apparatus for the continuous production of lead oxides in the dry state comprising a drum, means for feeding pieces of metallic lead to said drum, a conduit extending into said drum and connected to said source of supply of air under pressure, a plurality of nozzles connected to said conduit for causing said air to impinge upon said metallic lead pieces within said vessel whereby the surfaces of said pieces are oxidized, means for rotating said drum to grind said oxide from said metallic lead pieces, an ejector for removing said air and said oxide from said drum, means interposed in the path of travel of said air and powder for separating a portion of said powder from said air, and a collector for removing the remainder of said powder from said air.

8. Apparatus for the continuous production of lead oxides in the dry state comprising a drum, a conduit connected to a source of supply of air under pressure and extending into said drum, a plurality of nozzles connected to said conduit for causing said air to impinge upon said metallic lead pieces within said drum, means for rotating said drum, an outlet for said drum, an ejector for blowing said product from said drum through said outlet and a collector connected to said last named means for supplying said product from said air.

9. Apparatus for the continuous production of a product including litharge in a dry state comprising a vessel rotatable on axes and means extending through an axis for feeding pieces of metallic lead to said vessel, a conduit for feeding an oxidizing gas under pressure to the lower part of said rotatable vessel, said vessel having an outlet above the zone of impact between the oxidizing gas and the lead pieces in the vessel, whereby said oxidizing gas oxidizes the surface of the lead pieces and then blows the powdered lead oxides upwardly and outwardly from said surfaces, means for rotating said vessel, a chamber having a conduit communicating with said rotatable vessel, said chamber having vertically extending fabric filters in its upper portion and a lower portion below said filters into which said oxides may slide off and fall from the filters to be further oxidized to litharge and a conduit from the filters to conduct away the oxidizing gas separated by the filters from said oxides.

10. Apparatus for the continuous production of a product including litharge in a dry state comprising an apparatus including a vessel in the form of a drum, means for feeding pieces of lead into the drum, means for rotating the drum to cause frictional movement between said pieces, means for supplying under pressure an oxidizing gas to the interior of the drum so as to act on said pieces to form a coating of lead suboxide thereon and to remove from the pieces the powder formed by the abrading action of the pieces against one another, and means associated with said apparatus in which said lead suboxide may be converted into litharge while still in its dry state.

11. Apparatus for the continuous produc-

tion of litharge in a dry state comprising an apparatus including a vessel in the form of a drum, means for feeding pieces of lead into the drum, means for rotating the drum to cause frictional movement between said pieces, means for supplying under pressure atmospheric air to the interior of the drum in suchawise as to act on said pieces to form a coating of lead suboxide thereon and to take up and remove from the pieces the powder formed by the abrading action of the pieces against one another, and means associated with said apparatus whereby said lead suboxide is converted into litharge, and means for receiving the product collected from said apparatus

In testimony whereof I have affixed my signature.

GENZO SHIMADZU.

PLAINTIFFS' EXHIBIT NO. 61.

Patent No. 60825 (Public Notice No. 52079)
Classification No. 144 (6) oxidized products.
Date of Application—February 3, 1923.
Public Announcement—August 15, 1923.
Patent Issued—June 19, 1924.
Patent Owner (Inventor)
Genzo Shimiazu
420 Todoin goike Noboru Funaya Street
Jokyo ku, Kyoto.
His representative (attorney)
Morio Nakamatzu and two others.

DETAILED DESCRIPTION

Method of Manufacturing Lead Suboxide Powder Containing Metallic Lead

Character of the Invention and Gist of its Object

This invention is an improvement over Patent No. 41728 and consists of a method of manufacturing a fine powder of lead suboxide containing metallic lead by putting lumps of metallic lead or a coarse powder inside a rotating vessel, and while maintaining the temperature of the metallic lead above 60° Centigrade slowly rotating and grinding it to powder by the rubbing. Its purpose is the acceleration of the oxidation of metallic lead by a rise in temperature to form a layer of lead suboxide on the surface, and consequently augment the rubbing action and increase the manufacturing efficiency of fine powder.

Detailed Explanation of the Invention

Although when metallic lead is exposed to air, the surface is gradually spontaneously oxidized, the rate of oxidation is very slow. But as the temperature is raised the rate of oxidation is conspicuously increased. According to

experiment when the temperature reaches 60° Centigrade the phenomenon of oxidation is apparent and at approximately 160 degrees centigrade the surface already presents the appearance of lead suboxide. This invention utilizes this fact and is an improvement over the original Patent No. 41728. It provides for the manufacture of fine powder of lead suboxide containing metallic lead powder by placing lumps of metallic lead or coarse powder inside a rotating vessel maintaining said metallic lead at a temperature above 60° C. in an atmosphere of air or other oxidizing gases, rotating the vessel, causing lead suboxide to form on the surface of the metallic lead and alternately grinding and removing this as it forms.

In this invention the heat of friction, or the heat of reaction due to oxidation of the lead or both are used to increase the temperature of the metallic lead, and there is no bother in supplying external heat such as can be induced from electric heaters, gas heaters or other sources of heat. It is only required that the raw material of metallic lead be kept above a temperature of 60° centigrade in an atmosphere of air or other oxidizing gas. But in case heat produced by the process of this invention, like heat of friction and heat of reaction, are used, some device for maintaining the temperature had better be made to prevent dissipation of the heat resulting from conduction and radiation. Moreover, at this time, of course, by adjusting the rubbing surfaces and pressure by the number of metallic balls, and regulating the rate of revolution of the vessel, the amount of heat can be controlled.

In this invention the maintained temperature of the raw metallic lead material accelerates the oxidizing action so that a coating of lead suboxide is quickly found on the surface, and said layer of lead suboxide is readily ground to the state of a fine powder. The surface of newly exposed metallic lead is then changed to lead suboxide and as a result of alternately, or successively grinding and removing, not only is a great deal more of the product formed than by the invention of the original patent, but the follow-

ing results can be listed: (1) Since oxidation of the surface of the raw lead material is maintained in accord with the grinding action, there is little waste of power and the manufacturing efficiency can be very greatly increased. (2) By regulating the temperature the proportion of lead suboxide powder and metallic lead powder changes, so the observed specific gravity of the product and the condition of the particles can be changed as one desires. (3) Finely powdered lead suboxide containing finely powdered metallic lead like the product of this invention is chemically very reactive in comparison with pure metallic lead powder or lead suboxide; when the material is further oxidized in this way forming lead peroxide or litharge and it is supplied as the paste material for electrodes of storage batteries, the results are very good.

One example of its practical application will now be pointed out.

Four small holes about ⅛ inch in diameter are bored in every square inch of surface through the curved walls of a cylindrical iron vessel of diameter about 60 inches and length about 60 inches and whose outer wall is made of asbestos coating or other heat insulating material and so constructed that it can be rotated. Two hundred fifty kwans of metallic lead balls approximately 1 inch in diameter are thrown in, and the vessel rotated at about 25 revolutions per minute while air or other oxidizing gases are made to circulate within the vessel. When the temperature of the metallic lead within the vessel is maintained at 60 degrees C. or above, the surface of the metallic lead is readily oxidized and a coating of lead suboxide formed, said lead suboxide coating being ground off and removed by the frictional rubbing of the metallic lead balls on one another and frictional rubbing of the metallic lead balls on the inner walls of the vessel. The newly exposed metallic lead surface is then oxidized and successively and continuously a fine powder can be formed.

In this invention hard balls, like steel balls, can be thrown inside the rotating vessel with the metallic lead ma-

terial and assist in the frictional rubbing, and a blast of air or other oxidizing gas can be forced into the rotating vessel or these currents of gas can be set up by means of suction.

Mutual Relation of the Inventions

This invention is an improvement of the original patent No. 41728 and strikes at the practical application. The case of using small holes bored in the curved walls of a rotating vessel was included and used in patent of addition No. 42562. Moreover, the throwing of steel balls or other steel-like balls into a rotating vessel with the metallic lead was used in patent of addition No. 42564. Presumably as compared with these patented inventions the present invention accelerates the grinding action and very greatly increases the manufacturing efficiency of the product by especially maintaining the metallic lead material at the proper temperature during the formation of lead suboxide.

Scope of Patent Claim

In order to achieve the object recorded above, a method of manufacturing lead suboxide powder containing metallic lead powder is claimed, a special feature of which is putting lumps of lead or coarse powder in a rotating vessel, and rotating the vessel while maintaining the lead above 60 degrees centigrade in an atmosphere or air or other oxidizing gases.

Additional Claims:—

(1) In order to achieve the purpose of the above record, a method of manufacturing lead suboxide powder containing metallic lead is claimed, in which a constant temperature arrangement is set up in a rotating vessel or container, lumps of lead or coarse powder are thrown into it and the vessel rotated while the temperature of the metallic lead is maintained above 60 degrees centigrade.

(2) In order to achieve the purpose listed above, a method of manufacturing lead oxide powder containing metallic lead is claimed, by throwing lumps of metallic lead

or coarse powder into a rotating vessel and rotating the vessel while maintaining the metallic lead material at a temperature of or above 60 degrees centigrade in an atmosphere of air or other oxidizing gas by means of the heat of friction or the heat of chemical reaction, or both.

(3) In order to achieve the object recorded above a method of manufacturing lead suboxide powder containing metallic lead is claimed as described under scope of patent claims No. 1 in which metallic lead is thrown inside a rotating vessel and a definite temperature maintained inside the vessel by supplying electrical heat, gas heat or some other suitable source of heat.

(4) In order to achieve the object of the above record a method of manufacturing lead suboxide powder containing metallic lead is claimed as described under Scope of Patent Claims No. 1, in which lumps of metallic lead or coarse powder are placed inside a rotating vessel, this is kept at a temperature above 60 degrees centigrade and the vessel rotated while air is passed through it.

DEFENDANT'S EXHIBIT NO. 78.

7-24-17

LEAD DUST MANUFACTURE
ANALYSIS OF RESULTS OF EXPERIMENTS

PRODUCT
- (A) Rate produced
  - Directly
    - (D) Revolutions per minute
    - (E) Hardness of lead
  - Indirectly
    - (F) Load in drum
    - (G) Room Temp. & Ventilation
- (B) Oxidation
  - Directly:—(E)—Hardness of lead
  - Indirectly
    - (H) Temp. of & ventilation thru machine
    - (I) Time in machine
    - (J) Mesh of screen
    - (K) Length & angle of delivery tube
- (C) Apparent Sp. Gr.
  - Directly:—(B) Oxidation
  - Indirectly:—(L) Fineness of material
    - (E) Hardness of lead
    - (D) Rev. per min.

NOTE:—"Directly" as used above indicates that, other factors remaining constant, the property (P) of the product is a direct simple function of the factor (X) i. e. P = X times a constant. Similarly "Indirectly" indicates an indirect or involved function.

Altho, strictly speaking, the "rate of production" is not a property of the product, it simplifies the analysis to treat it as such, thus helping to bring out its importance and degree of independence.

Practical Limits of above Quantities:—

"A" = 40-60 lbs. per hour.

"B" = 60-80% PbO

"C" = 3. - 4. sp. gr.

"D" = 12.5-15 Rev. per min.

"E" = ——————Ordinary "St. Joe" lead seems to work well. "Doe Run" was quite unsatisfactory.

"F" = 1800-2400 lbs.

"G" = 60-80° Fahr. This emphasizes the necessity of adequate ventilation during warm weather.

"H" = 165-185° Fahr. The greater the internal ventilation thru the machine the greater the speed at which it can be operated without exceeding its temperature limit, thus increasing the ease of control and the output. The German design did not show this.

"I" = ——————

"J" = 60 mesh to ——————. 60 is the fine limit, as under some conditions the meshes tend to clog. It is possible to produce useable material without the screen, but this so narrows the other limits that it does not appear very practical to do away with it entirely. Note that the screen does not determine the fineness of the material, but its *only function* appears to be to delay the delivery of the material and hence to assist in its proper oxidation.

"K" = Besides delivering the material, this tube plays an even more important part in the oxidation than the screen. If the tube is too short and its angle with the horizontal too steep, the material is delivered in a hot, semi-oxidized condition, and

will be quite apt to get on fire in the container. On the other hand too long a tube with insufficient slope is apt to become clogged with material.

"L"_____.

GENERAL OPERATIONS.

The general rules of operation during experimental runs are so well understood that it does not seem necessary to go into them in detail. If, however, it is decided to run the mill for a continuous output there are some points to be emphasized.

Run at the highest speed and load consistent with a useable product.

Control the character of the product as far as possible by the external and internal ventilation systems, installing fans if necessary.

It brings down the temperature better and diminishes the output less, to reduce the load rather than the speed.

It is safe to judge the oxidation by the color and the tendency to heat in the container. Under normal conditions the container, at the level of the material, is too hot to bear the hand on, but not hot enough to scorch the skin if touched quickly. Normal material has a color ranging from a velvety bluish green to a medium light yellowish green.

STORING THE PRODUCT.

Samples of lead dust made nine months ago and stored in glass stoppered bottles show apparently no change, whereas the same materials turned to litharge in less than a week when stored in paper bags.

Hence the successful dry storage of the material depends purely on the tightness of the container. The present steel packages would probably be entirely satisfactory if they were provided with heavy steel or cast iron top rims and with proper rubber or lead gaskets.

Similarly any fluid which tends to prevent the free access of air will delay the oxidation. It is possible, but does not look very practical, to store under water. It should be noted in this connection that damp material oxidizes more readily and more completely than dry material.

No definite limit of oxidation has yet been established beyond which the material does not make good positives, and experiments should be made to determine this.

It seems likely that material which has kept badly in storage will make entirely normal negatives and it would be well to make a complete series of experiments along this line.

WEK.L
7-24-17

DEFENDANT'S EXHIBIT NO. 111.

Patent No. 41728
Classification No. 154.
Date of application—November 21, 1920.
Patent issued—February 13, 1922.
Patent owner (inventor)

Genzo Shimadzu
420 Todoin Goike Noboru Funaya Street
Jokyo ku, Kyoto, Japan

DETAILED DESCRIPTION

A Method of Manufacturing Very Reactive Lead Powder

Character of the Invention and Its Main Object

This invention consists in placing pieces of metallic lead inside of a rotating vessel, rotating the vessel, and grinding them to bits by means of the frictional rubbing of the lumps of lead on one another and on the inside walls of the vessel, to manufacture fine lead powder. Its object is the simple and inexpensive manufacture of chemically reactive, irregularly shaped lead powder without the process of crushing.

Detailed Explanation of the Invention

In the manufacture of metallic powders up to the present time, the usual procedure has been either to crush by the method of crushing and pounding or, as in the method of manufacturing zinc powder, to mix the vapors of the metals with air etc. and condense them into powder-like solids; however, these products are not only large and rough granules whose surfaces are changed to a hard and tough character, but the former product shows a pressed together condition so that it is very difficult for it to act readily with chemical reagents, and the surface of the latter is easily oxidized and thus has the defect of being covered with oxidized material. But even supposing this is mashed and formed into a powder, it is very large and rough and due to cracking, etc. the

purity of the product is in danger of being very greatly reduced. On this account, no matter what is done, as might be expected from these inventions, it is impossible to supply a specific chemical material. The present invention is not dependent on these methods and is an application of the use of the well-known rotating vessel used in pulverizing rocks. That is to say, lumps of lead are thrown into a rotating vessel and ground into a powder by means of the frictional rubbing of the lead lumps on one another and on the inner walls of the rotating vessel, due to rotation of the vessel; moreover, the degree of fineness of the lead can be conveniently governed by the amount of lead lumps put in.

One example of the manufacture of lead powder by the method of the present invention will be given.

An iron cylinder 60 inches in diameter and 60 inches in length and which can be made to rotate is mounted horizontally and 250 Kwans of lead balls having a diameter of one and one half inches thrown into it; then during the time it is rotated at about 25 revolutions per minute, the lead balls rub on one another and on the inner walls of the vessel, so that they are gradually reduced by friction to small particles, and in an hour's time about 10 Kwans of irregular, fine powder is made and can be collected.

On account of the fact that the metallic powder manufactured by the method of the present invention is very irregular in shape and exceedingly fine with a comparatively large surface area, it can oxidize readily and, depending on the amount of spontaneous combustion produced, it is sometimes necessary to dissipate the head of friction by installing a cooling system in the rotating vessel.

An important point of this invention is the reduction of lumps of lead to fine particles in a rotating vessel by their frictional rubbing on one another and on the inner walls of the vessel, while it is rotating, without crushing or smashing the metals as in methods used heretofore; and in contrast to the previous methods, this has the following special features:—

(1) The power required is small, the process is simple and the degree of fineness of the powder can be conveniently controlled;

(2) The degree of fineness is very different; that is, the product resulting from this invention is very fine and, moreover, the losses in the degree of purity are small;

(3) The chemical action is very violent and the powder can be oxidized in air, for on experiment the condition of the particles is irregular, they are rough and the surface area is very large, and because of the amount of natural ignition the product can be very economically used in various chemical materials, such as litharge and as electrode material in storage batteries and paint material.

(4) The product of this invention is very effective as an intermediate catalytic with powerful contact action, as a material for reducing the polarity of a battery and a material for restoring the polarify of a battery, and as a material for supplying oxygen.

Scope of Patent Claims

(1) In order to achieve the purpose recorded above, a method of manufacturing chemically reactive lead powder is claimed, a special feature of which is throwing lumps of lead into a rotating vessel and by rotation of the vessel grinding lumps of lead to small pieces.

(2) In order to achieve the purpose as recorded above, a method of manufacturing chemically reactive powder is claimed which consists in placing round lumps of lead in a rotating vessel and reducing them to small particles by means of the frictional rubbing of the balls on one another and on the inner walls of the vessel when this is rotated.

DEFENDANT'S EXHIBIT NO. 112.

Patent No. 42563 (Addition to Patent No. 41728)
Classification No. 154
Date of Application—November 27, 1920
Patent Issued—May 10, 1922
Patent Owner (Inventor)

Genzo Shimazu
420 Todoin Goike Noboru Fnaya Street,
Jokyoku, Kyoto, Japan.

DETAILED DESCRIPTION

A Method for the Continuous Manufacture of Very Reactive Lead Powder

Character of the Invention and its Main Object

This invention is an improvement of that covered by Patent No. 41728 and consists of a method for manufacturing lead powder which is very reactive chemically by placing lumps of metallic lead inside a rotating vessel, and, while rotating the vessel to reduce the lead to small particles by frictional rubbing, blowing in some air or other inactive gases to cause the small particles to fly out of the vessel; and then collecting them. The purpose or object briefly is to obtain (extract) a product, the measured and observed specific gravity of whose small particles is fixed, to prevent a decrease in the rubbing action (or friction), and to increase the efficiency of the production.

Detailed Explanation of the Invention

This invention is an improvement over the one covered by patent No. 41728 and consists of blowing air or some other kind of inactive gas like nitrogen into a rotating vessel, while it is rotating, to forcibly blow out all the particles ground sufficiently small, thus avoiding considerable trouble and eliminating the decrease of the frictional action due to an accumulation of the powder inside the vessel. At the

same time, the size of the particles can be governed by the velocity of the gas blowing in. Here is given a specific case:—

A hollow iron cylinder 60 inches in diameter and 60 inches in length and which can be made to rotate is constructed horizontally. Within the cylinder is placed air jet pipe with small holes pierced in it. A door for inserting the material is made in one side of the cylinder, and a door for removing the finished product is made in the other side. Lead balls having a diameter of 1½ inches are supplied to the cylinder through the first door at the fixed rate of about 27 kan per hour continuously. While the cylinder is rotating at the rate of 25 revolutions per minute, air at a pressure of 2.5 pounds to the square inch is jetted out from the air jet tube, and since the lead balls are gradually ground to small pieces these are blown out through the outlet door to the outside of the cylinder and directed to a suitable place and collected. In this manner, 27 kan of lead powder having no regular or definite shape with an ordinarily observed density or specific gravity of approximately 2.3 can be produced per hour.

Fine, porous, irregularly shaped lead powder made in conformity with the original patent No. 41728 is liable to ignite spontaneously due to the heat of friction on the inside of the rotating vessel. But this defect is not only eliminated by the present invention by blowing in air or some other inactive gas with a resultant cooling effect, but the decrease in the frictional action due to an accumulation of the small particles which are produced is avoided because these particles are blown outside the rotating vessel; moreover, since the work is done continuously, the efficiency the manufacturing process can be very much increased.

While the main point of this invention is the placing of lumps of metallic lead inside the rotating vessel and due to its rotation alone, without crushing, reducing the size of these lumps, a special feature of the invention is the blowing of the small particles out from the vessel by means of

the air or other gases. The merits of the invention are as follows:

(1) The small particles produced during the frictional rubbing are continuously forced out from the vessel by the currents of air and gas, and due to the cooling effect, the product is not liable to attack by the air occasioned by the heat generated during the work;

(2) There is no reduction in the frictional action due to the accumulation of small particles, and the grinding efficiency can be increased;

(3) It is easy to regulate the size of the product, since, by adjusting the force of the incoming currents, particles of a fixed density can be blown out by fanning;

(4) The raw material can not only be supplied at a constant rate and the work go on continuously because there is no trouble in opening the vessel, for the product is forced out by the strength of the currents, but the conditions on the inside of the rotating vessel con be approximately controlled and the frictional action made constant, so that a product can be obtained whose measured and observed specific gravity (density), etc., is always constant.

Scope of Patent Claims.

(1) In order to achieve the object recorded earlier in this record, a method of manufacturing chemically reactive lead powder is claimed, a special feature of which is throwing lumps of lead into a rotating vessel, and blowing currents of air or other inactive gases into the vessel during rotation to force the small particles produced by rubbing out of the vessel.

(2) In order to achieve the purpose recorded above, a method of manufacturing chemically reactive lead powder is claimed, as stated in the previous paragraph, which governs the size of the particles by means of the velocity of currents of inblówing air.

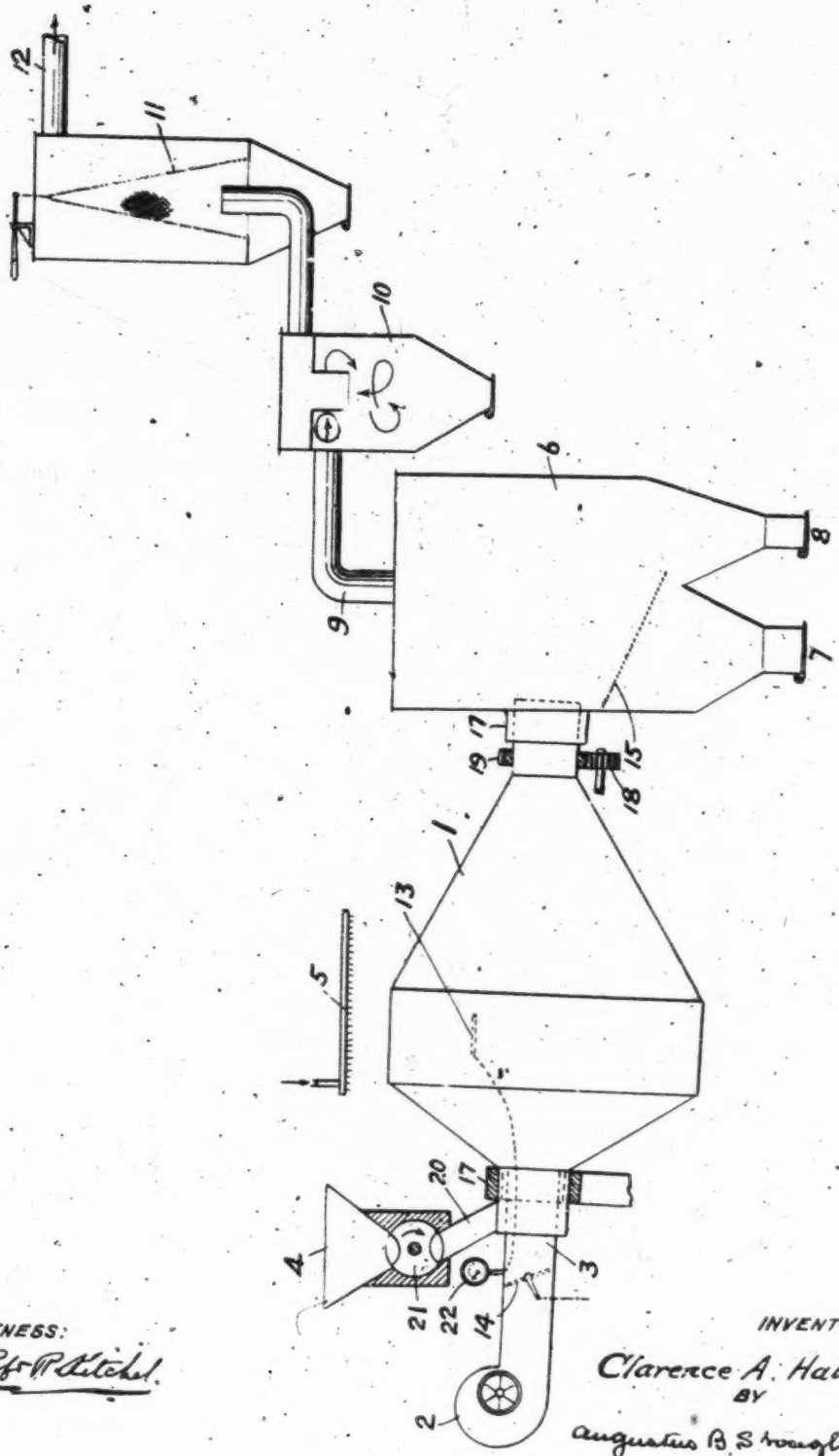
(3) In order to achieve the purpose recorded above, a method of manufacturing chemically reactive lead powder is claimed, as stated in the preceding paragraphs, which provides for continuously or periodically supplying raw material in the form of lumps of lead at a given rate, and blowing out the finished particles by the force of the wind so that the work is done continuously.

July 3, 1928. 1,675,345

C. A. HALL

APPARATUS FOR MAKING LEADEN POWDER

Original Filed March 29, 1924



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Patented July 3, 1928. 1,675,345

UNITED STATES PATENT OFFICE.

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APPARATUS FOR MAKING LEADEN POWDER.

Application filed March 29, 1924, Serial No. 702,890. Renewed December 2, 1927.

The principal object of the present invention is to provide an apparatus for use in the manufacture of leaden powder of the order of lead oxides. Another object of the invention is to provide such an apparatus with appropriately independent controls whereby the character and quality of the product in respect to oxygen content can be varied to establish different products and to permit of the manufacture of any established product in such a way that it is of uniform quality. A further object of the invention is to provide for the dissipation of the heat evolved by quantity production in excess of the heat permissible for the successful accomplishment of the chemical reaction. Additional objects of the invention will appear from the following description at the end of which the invention will be claimed.

The invention comprises the improvements to be finally claimed and presently described in connection with the accompanying drawings forming part hereof and in which the single figure is a view partly in section, but principally in side elevation, schematically or diagrammatically illustrating features of apparatus embodying or containing one form of the invention.

In the drawing, 1 is a hollow drum of the general form of reversely disposed conic frustums extending from a cylindrical center portion. This drum provides a closed curved wall. The drum is revoluble about a substantially horizontal axis. However, as shown, the axis is slightly inclined from left to right in the direction of feed of the solid material. 17 indicates bearings in which the drum is revoluble. Toothed gearing 18 represents a means for driving the drum and the part 19 of this gearing which is carried by the drum is shown as broken away for the sake of clearness although it extends all the way around the surface of the drum. 4 is a feeder at the inlet end of the drum and it communicates with the interior of the drum by way of the passage 20 and through the hollow trunnion of the drum. The rotary pocketed element 21 is a means for enclosing the feeder against the entrance of air while permitting of the introduction of balls or lumps of lead into the drum. 6 is an enclosed delivery hopper at the outlet end of the drum and it communicates with the interior of the drum through a hollow trunnion. The delivery hopper 6 is provided with stoppered outlets 7 and 8 and with a screen 15 which operates to deliver fine material, the finished product, at the opening 7, and coarse material at the opening 8, and this coarse material, when produced and if desired, may be returned to the interior of the drum for further treatment. 5 is a means, shown as a water spray device, for applying cooling fluid to the exterior of the curved wall of the drum. The fan 2, the conduit 3, and the pipe 9 constitute a means for passing a stream of air axially through the drum in either direction and, as shown, the direction is from left to right. 10 is a dust catcher, and 11 is a dust bag having an outlet 12 to the atmosphere, and these dust catching devices are arranged in series with the outlet of the pipe 9. 14 is a damper for controlling the volume of air flowing through the drum, and 13 is a thermometer arranged generally centrally of the interior of the drum and provided with a dial 22. In general there is provided an air containing rumble 1 rotated at a speed appropriate for quantity production, and there are means for dissipating heat evolved by the action of the rumble on lead balls or lumps contained therein in excess of the heat appropriate for the chemical reaction. These heat dissipating means operate independently of the speed of revolution of the rumble, and since they comprise air control and cooling fluid application they are independent of each other.

In use the air containing rumble 1 supplied with balls or lumps of lead is rotated at a speed determined for quantity production of the leaden powder. This results in the evolution of heat in excess of that appropriate for the formation of powdered lead oxide. The excess heat is dissipated either by the application of fluid to the exterior of the rumble, for example at 5, or by control of the volume of air as at 14, or by the combined use of both of these instrumentalities. When the rumble is of the form shown, it is necessary to feed lead balls or lumps into it, in order that the powdered oxide will escape from it into the delivery hopper 6, from which it is removed as by way of the outlet 7 for use. The dust caught in the dust catchers 10 and 11 may also be collected and used. If coarse material is removed from 8 it can be returned to the interior of the rumble 1 for further treatment. The thermometer 13 is a means

for ascertaining the temperature in the interior of the drum 1, so that the necessary controls 14, 5, or both, can be regulated. In some cases the speed of revolution of the drum can be reduced in order to avoid the evolution of too much heat for the successful production of leaden oxide but reduction of the speed of revolution of the drum 1 is accompanied by diminution in the quantity of production.

It will be obvious to those skilled in the art to which the invention relates that modifications may be made in details of construction and operation without departing from the spirit of the invention which is not limited as to those matters or otherwise than as the state of the prior art and the appended claim may require.

I claim:

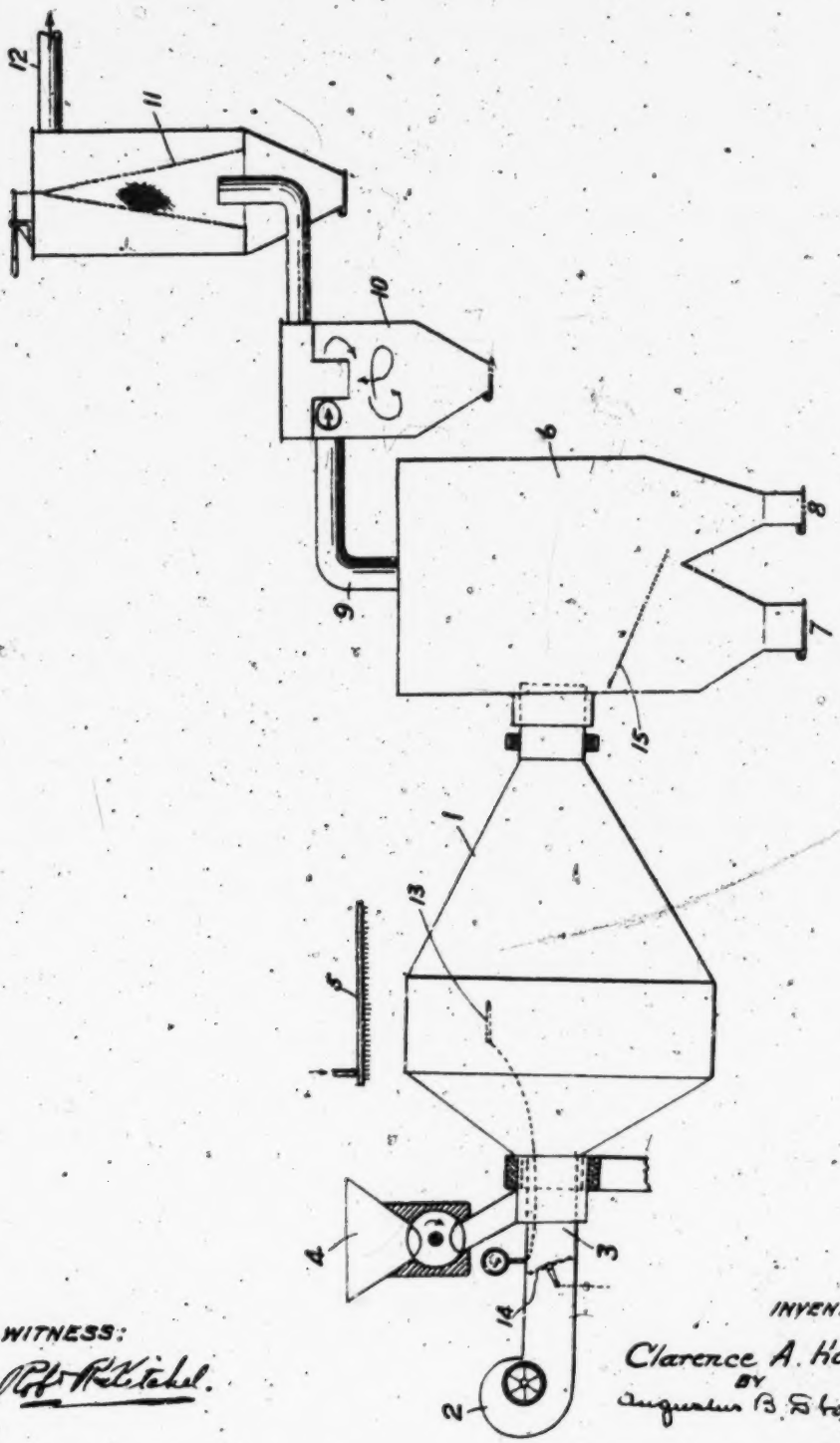
Apparatus for making leaden powder comprising in combination a hollow drum of the general form of reversely disposed conic frustums and having a closed curved wall and being revoluble about a substantially horizontal axis, means for rotating the drum, an enclosed feeder at the inlet end of the drum and in communication with the interior of the drum, an enclosed delivery hopper at the outlet end of the drum and in communication with the interior of the drum, controlled means for spraying cooling fluid onto the exterior of the drum, and controlled air connections for passing a stream of air axially through the drum, said cooling fluid means and said air connections being independently operatable for dissipating the excess of evolved heat over the limited degree of heat appropriate for the success of the chemical reaction between the air and lead.

CLARENCE A. HALL

Nov. 22, 1932. C. A. HALL 1,888,823

LEAD OXIDE POWDER AND METHOD OF MAKING THE SAME

Original Filed March 29, 1924



WITNESS:

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UNITED STATES PATENT OFFICE

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LEAD OXIDE POWDER AND METHOD OF MAKING THE SAME

Application filed March 29, 1924, Serial No. 702,889. Renewed December 24, 1928.

Objects of the present invention are, first, to provide a lead oxide powder of the order of lead oxides used extensively in the arts but much less expensive to produce and capable of replacing them for many purposes such as in the manufacture of storage batteries and paints and in some cases with beneficial and improved results; and second, to provide an expeditious, comparatively inexpensive and reliable method of making such lead oxide powder of substantially uniform qualities.

Other objects of the invention will appear from the following description and the invention will be claimed at the end hereof.

In the following description reference will be made to the accompanying drawing comprising a single figure and illustrating, partly in section but principally in side elevation, apparatus by means of which the product can be made in accordance with the method.

The product is an amorphous fine powder. The degree of its fineness can be illustrated by saying that it will pass through a 200 mesh. The powder is olive gray in color and it is unstable or highly chemically reactive if exposed to air, more particularly moist air of the atmosphere, and spontaneously oxidizes or approaches litharge. The specific weight (weight of a given volume of powder in terms of the same volume of water) of the product is approximately from 2.10 to 2.25, and it contains from 50% to 80%, or the major portion, of oxide calculated as litharge. The product in sealed drums, such as are usually used for lead oxides, will remain stable for a week or so. Some of the product is absorbed in a dilute solution of acetic acid and some of it remains as metallic lead of spongy form. The quality of the product is very uniform and when used for paints its instability and property of oxidizing in the air is of value and its uniformity of quality is of value not only in the paint industry but also in battery production. The product differs from the five well known oxides of lead although it may be a mixture of them or some of them and may possibly contain, in addition to metallic lead, lead in somewhat intermediate state or condition or lead suboxide. While a number of its identifying characteristics have been set forth, the clearest and best way to identify the product appears to be reference to its process of production or to the process of which it is the result.

In the drawing 1 is a double cone mill of the Hardinge type and it is revolved around an axis in general horizontal but very slightly inclined to the horizontal towards its outlet end. 2 is a blower having a discharge 3 into the casing 1. 4 is a hopper for feeding balls or lumps of lead into the mill and it is of the type that excludes the entrance of air. 5 is a device for putting water on the exterior of the mill. 6 is a discharge hopper fitted with a stoppered outlet 7 for the leaden powder and with a stoppered outlet 8 for coarse material which is returned to the mill. The hopper 6 is fitted with an air off-take 9 which may include a dust catcher 10 and a dust bag 11 from which air escapes at 12. The devices 10 and 11 serve as a means for recovering some of the product. 13 is a thermometer device for ascertaining the temperature existing in the mill. 14 is a shutter for controlling the air supply. The temperature can be controlled by the discharge of water at 5 and also by adjustment of the damper 14, and adjustment of the damper 14 is one way in which the supply of air and consequently the available oxygen content at the reaction zone can be adjusted. 15 is a screen.

While the described apparatus is subject to considerable modification and change, for example, in the direction of travel of the air, still it will be referred to in describing the method of the invention which may be said to consist in subjecting lumps or balls of metallic lead to mutual attrition and oxidation at a temperature limited to approximately under the melting point of lead and in the presence of a supply of air.

For the sake of further description it may be said that good results can be produced as follows: With a drum 1, six feet in diameter and ten feet in length, fourteen revolutions per minute are appropriate. One hundred and fifty cubic feet of air per minute are passed through the mill which is charged with 19,000 pounds of balls of metallic lead

of ⅜ inch in diameter. Substantially 480 pounds per hour of product are produced and somewhat less than 480 pounds of lead balls are fed into the mill per hour having in mind the increase in weight due to the oxidation of lead. The temperature is kept at less than 360° F. by water discharged from 5 onto the mill. It may be said by way of illustration that in the reaction zone, which may be taken to be located generally at the center of the mill, the air is substantially 6% oxygen content, whereas when introduced from the atmosphere it is about 20% oxygen content. From the foregoing description it will be apparent that the pieces or balls of metallic lead are reduced to powder by mutual attrition and that the powder is oxidized under controlled temperature and available oxygen conditions.

It is not the intention to limit the invention in respect to the size of the lumps or balls of metallic lead or to the exact size and speed of the mill, or to the quantity of the air, or to the temperature of the reaction, as they may be varied in accordance with practical requirements. Control of these factors, however, is the spirit of this invention, whereby any product once established may be kept substantially uniform in quality. The direction of the travel of the solid material undergoing process is generally axial of the mill and so is the direction of the stream of air, whether it flows counter to or with the solid material.

The apparatus shown and described is not claimed herein because it forms the subject-matter of my application, Serial No. 702,890.

The invention is not limited to the details of procedure herein descriptively referred to nor in respect to matters of mere form, nor otherwise than as the prior art and the appended claims may require.

I claim:

1. As an article of manufacture an amorphous lead oxide powder of olive gray color and of specific weight approximately 2.15 and being the product of the mutual attrition of metallic lead lumps at a temperature under 360° F. and in the presence of a controlled stream of air.

2. The process of making lead oxide powder of olive gray color and of amorphous structure which consists in subjecting balls or lumps of metallic lead to mutual attrition by rumbling them while confined by the closed wall of a vessel in a stream of air passing through said vessel, and controlling the temperature by the application of cooling fluid to the exterior of said wall.

3. The process of making lead powder of the order or lead oxides and of amorphous structure which consists in subjecting balls or lumps of metallic lead in a dry state or condition to mutual attrition in a stream of air thereby evolving heat in excess of that appropriate for the reaction and limiting the resultant heat to a degree appropriate for the reaction by controllably dissipating heat in excess of that appropriate for the reaction, continually introducing fresh supplies of lumps or balls, and drawing off the product.

4. The process of making an oxidized lead powder which consists in establishing and maintaining a triturating and oxidizing zone or region within a vessel closed to the atmosphere by rumbling a mass of lumps or balls of lead in a dry state or condition in said vessel and by passing a regulated stream of air axially therethrough and by controlling the temperature thereof, feeding lumps or balls of lead to said region, and axially withdrawing oxidized powder from said region, substantially as described.

CLARENCE A. HALL.

CLERK'S CERTIFICATE.

UNITED STATES OF AMERICA,
EASTERN DISTRICT OF PENNSYLVANIA, } *Sct.*
THIRD JUDICIAL CIRCUIT,

I, WM. P. ROWLAND, Clerk of the United States Circuit Court of Appeals for the Third Circuit, DO HEREBY CERTIFY the foregoing to be a true and faithful copy of certain of the original exhibits submitted to this Court at the argument before it in the cases of The Electric Storage Battery Co., Defendant-Appellant, v. Genzo Shimadzu and Northeastern Engineering Corporation, Plaintiff-Appellee, and Genzo Shimadzu and Northeastern Engineering Corporation, Plaintiff-Cross-Appellant, v. The Electric Storage Battery Co., Defendant-Cross-Appellee, (Nos. 6309 and 6336) on file, and now remaining among the records of the said Court, in my office.

IN TESTIMONY WHEREOF, I have hereunto subscribed my name and affixed the seal of the said Court, at Philadelphia, this twenty-eighth day of October, in the year
(Seal) of our Lord one thousand nine hundred and thirty-eight and of the Independence of the United States the one hundred and sixty-third.

WM. P. ROWLAND,
Clerk of the U. S. Circuit Court of Appeals, Third Circuit.

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